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X-RAY PHOTOELECTRON SPECTROSCOPY SURFACE STUDIES OF ACTIVATED CARBON

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ASC, ASC treated with triethylenediamine (TEDA), and BPL carbons have been analyzed using X-ray photoelectron spectroscopy (XPS). Carbon samples were analyzed both as received from Calgon in 12-30 mesh particles and crushed to <325 mesh. Results indicate that copper is present on the carbon primarily in the +2 oxidation state. XPS was used to determine Cr(VI)/total Cr ratios; details of this procedure were reported. ASC treated with TEDA possessed a greater fraction of chromium in the +6 oxidation state than did untreated ASC. Quantitative XPS analysis revealed that the external surface of the 12-30 mesh granules are rich in impregnants relative to the bulk phase.

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PREFACE

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X-RAY PHOTOELECTRON SPECTROSCOPY
SURFACE STUDIES OF ACTIVATED CARBON

1. INTRODUCTION

ASC Whetlerite is used for removal of reactive gases from streams of air. Of importance to the military is its ability to remove HCN, $(CN)_2$, CNCL and AsH_3 through reaction/chemisorption with impregnants, namely copper, chromium and silver. ASC Whetlerite is prepared through impregnation of charcoal granules with ammonium carbonate solutions of chromium(VI), copper(II) and silver salts. The speciation of the impregnants is not well defined. Pytlewski[1] has reported the existence of various copper-chromium complexes on ASC Whetlerite. These include $Cu(NH_3)_2CrO_4$, $Cu(NH_3)_4CrO_4$, $Cu_4(OH)_6CrO_4 \bullet xNH_3 \bullet yH_2$ and $CuOHNH_4CrO_4$; all of which contain chromium in the $+6$ oxidation state. Hammarstrom and Sacco[2,3,4] have studied ASC Whetlerite using both spectroscopic and wet chemical techniques. Their results indicate that copper is primarily in the $+2$ oxidation state, with small amounts of copper(I) and copper(0) detected. Approximately 80% of the total chromium was found to be present in the $+6$ oxidation state. For military applications, it is important that as much chromium as possible be in the $+6$ oxidation state. This is because Cr(VI) complexes on impregnated carbons have been directly linked to cyanogen chloride destruction.[1,5,6]

Treatment of ASC Whetlerite with triethylenediamine (TEDA) following impregnation is reported to improve protection against cyanogen chloride. The influence of TEDA on the protection of Whetlerite against cyanogen chloride has been investigated by Groose et al.[7] Their studies found that treatment of ASC with TEDA increased the protection for both fresh and aged samples. The reason for the improved performance upon treatment with TEDA was not investigated.

The objective of this study was to determine the oxidation state(s) of the impregnants and investigate whether a large fraction of the impregnants is located at the external surface of the carbon granules. Both ASC and ASC treated with TEDA (ASC-TEDA) will be analyzed in an effort to determine the role of TEDA in the improved reactivity of ASC.

2. EXPERIMENTAL METHODS

2.1 Materials.

ASC Whetlerite and ASC Whetlerite treated with triethylenediamine (TEDA) (lot numbers 1667 and 794, respectively) were obtained from Calgon Corporation (Pittsburgh, PA). These materials contain 8% copper, 3% chromium and 0.2% silver by weight in an activated carbon matrix. The ASC-TEDA sample contains 2% TEDA by weight. BPL carbon (lot number 7502) was also obtained from Calgon Corporation. BPL is similar to the ASC carbons but does not contain impregnants. All charcoal samples were received as 12-30 mesh (U. S. standard sieve) granules.

2.2   Equipment.

XPS spectra were recorded using a Perkin-Elmer Phi 570 ESCA/SAM system employing MgK-α X-rays. Samples were analyzed for carbon, oxygen, copper, and chromium. No silver could be detected. All spectra were recorded using the instrument settings listed in Table 1.

Table 1
XPS Instrument Parameters

Element	C 1s	Cu 2p	Cr 2p	O 1s
Energy range (eV)	285-265	974-924	590-560	535-515
Volts/step	0.10	0.10	0.10	0.10
Time/step (ms)	50	50	50	50
Scans	5	20	35	10

Acquisition time:	60 minutes
Anode power (W):	300
X-ray voltage (KV):	14
Pass Energy:	75
Anode type:	Mg

2.3   Sample Mounting.

Samples were analyzed as both granules (as received from Calgon) and as fine particles. The fine particles were prepared by gently crushing the granules and sieving to < 325 mesh. Samples of carbon are attached to stainless steel mounts using double stick tape. Carbon granules are placed onto the mount so that the entire surface is nearly covered.

The mounted sample was then placed into a vacuum oven and heated to between 50-65 °C for 5-10 minutes. This was necessary in order to remove adsorbed water and other impurities which will contaminate the analysis chamber. Following heating in vacuum, the mounted sample was then removed from the vacuum oven and immediately placed (while still hot) into the introduction chamber of the analysis unit. The introduction chamber was then evacuated using a turbomolecular pump (10^{-6} torr) for 30-90 minutes. Following evacuation, the sample was placed within the analysis chamber ready for analysis.

A test was performed to determine if the mild heating in the vacuum oven altered the sample (e.g., changes in metal oxidation state, atomic ratios, etc.). A sample of ASC carbon granules was evacuated within the introduction chamber for 40 hours prior to analysis. The extensive time was required to remove the adsorbed

phase and prevent contamination of the analysis unit. Subsequent analysis revealed no detectable changes in the spectra, indicating that the mild heating step did not alter the sample.

2.4   Binding Energy Determination:

All binding energies are reported referenced to the carbon 1s photoelectron peak at 284.6 eV[8]. Recorded binding energies were corrected for instrument scaling and sample charging. Instrument scaling deficiencies are caused by the energy region not being properly defined by the computer. This results in shifting the position of the photoelectron peaks associated with the elements comprising the sample. Unlike shifts in binding energy due to sample charging, shifts caused by improper instrument scaling are not sample dependent and are easily corrected algebraically through the use of a calibration standard (typically copper metal).

Correction of the recorded binding energies for improper instrument scaling was performed first. This was accomplished by analyzing copper metal and recording the binding energies of the carbon 1s, oxygen 1s, copper $2p_{3/2}$, copper $2p_{1/2}$ and the copper $3p_{3/2}$ photoelectron peaks. The binding energies of these peaks are reported along with their respective reference binding energies in Table 2:

Table 2
Recorded and Reference Binding Energies

	Recorded BE	Reference BE	Δ eV
$Cu3p_{3/2}$	68.0eV	74.9eV	-6.9
C 1s	279.8	284.6	-4.8
O 1s	528.4	530.5	-2.1
$Cu2p_{3/2}$	933.5	932.4	1.1
$Cu2p_{1/2}$	954.4	952.2	2.2

Note from the Table 2 that the differences between the recorded and reference binding energies (ΔeV) are not constant and differ by about 9 eV over the range of the data. This is not due to sample charging (as in the case of charging, the difference between the recorded and reference binding energies will usually be constant). These data indicate that the instrument scaling is not correct and that corrections have to be performed.

Figure 1 illustrates a plot of ΔeV versus the reference binding energy. Note that all points fall on a straight line. The equation for correcting the binding energy for instrument scaling is determined from a linear least squares fit of the recorded binding and the reference binding energies. From the data reported above, the equation used to correct for instrument scaling is as follows:

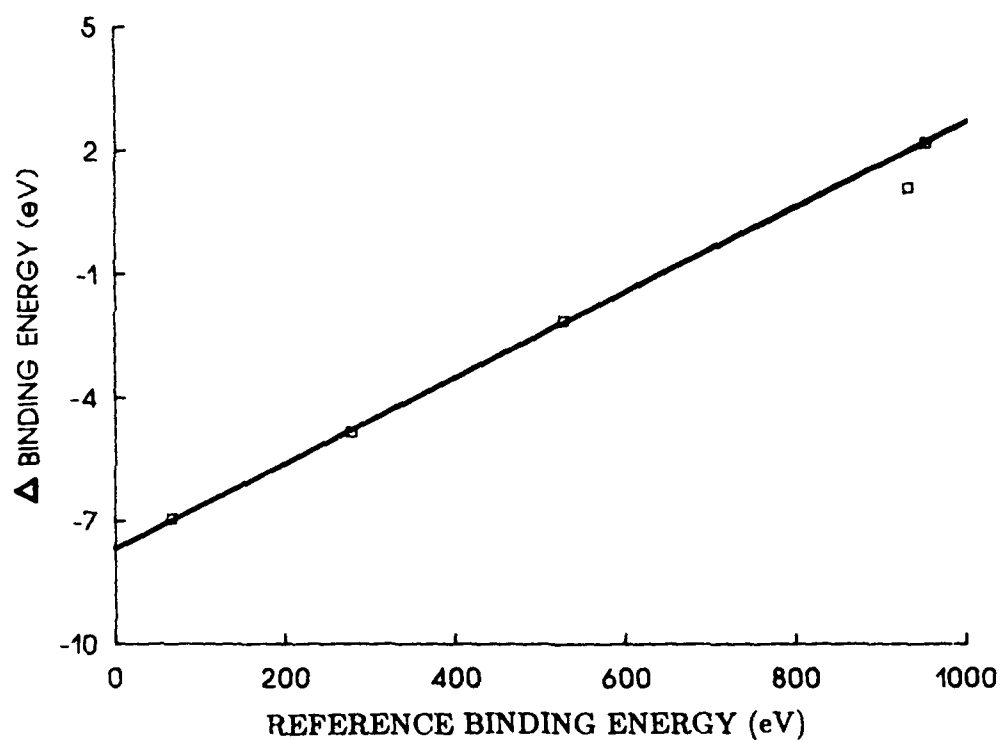$$\text{Corrected BE(eV)} = 0.9897(\text{Recorded BE}) + 7.62 \text{ eV} \tag{1}$$

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Figure 1. Difference Between the Recorded and Reference Binding Energy as a Function of the Reference Binding Energy as Determined from Analysis of Copper Metal.

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This equation was used to correct the recorded binding energies for instrument scaling for all samples analyzed in this study. Following this correction, the elemental binding energies must be corrected further for sample charging.

Charging of the sample results in a positive shifting of the photoelectron peaks. Charging will vary from sample to sample and corrections must be made so that different samples may be compared. This correction is performed by normalizing position of peaks of interest with respect to a reference peak (typically carbon) as follows:

$$BE\ C\ 1s\ (eV) - 284.6(eV) = \Delta BE\ (eV) \tag{2}$$

$$Corrected\ BE(eV) = Recorded\ BE(eV) - \Delta(eV) \tag{3}$$

Corrected binding energies are now utilized in determining chemical states of elements of interest.

2.5   Quantitative Analysis.

Quantitative XPS analysis provides information regarding elemental ratios at the exposed surface of the material. The relative quantities of each element are determined by dividing the integrated peak areas by a sensitivity factor associated with the individual peak. The relative amount of each element present at the surface of the sample may be compared by dividing the area of the element of interest with the area corresponding to the element making up the support. XPS sensitivity factors are supplied by the manufacturer and are based on the elemental cross sectional area and the mean free path.

Table 3
Sensitivity Factors

Element	Sensitivity Factor
Cu 2p	6.70
Cr 2p	2.30
C 1s	0.25
O 1s	0.67
Cl 2p	0.70
F 1s	1.00

2.6   Cr(VI)/Total Cr Determination.

Chromium(VI)/total chromium ratios were determined by subtracting the chromium spectrum of CrO_3 from the chromium spectrum of the impregnated carbons. CrO_3 was chosen as a representative Cr(VI) species. The CrO_3 spectrum was scaled so that the apex and baseline (about 527 eV) of the $2p_{3/2}$ peak

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corresponded to that of the activated carbon. Ratios of chromium (VI) to total chromium were then obtained subtracting from 1 the ratio of the area of the Cr $2p_{3/2}$ peak obtained following subtraction to the area of the Cr $2p_{3/2}$ of the corresponding carbon sample. Values obtained should be considered approximate due to errors involved with normalization and subtraction of peaks. An example of the results obtained following peak subtraction are illustrated in Figure 2.

3.   RESULTS

Figure 3 illustrates for comparison the XPS spectra of the copper 2p photoelectron region of ASC Whetlerite (as granules and crushed to <325 mesh), crushed ASC-TEDA and copper(II) oxide. The spectra corresponding to ASC-TEDA granules is similar to that of the crushed ASC-TEDA. Note from this figure that all peaks are at approximately the same position. The binding energy of the $2p_{3/2}$ peak (933.5±0.1 eV) along with the characteristic shake-up peaks, indicate that copper is in the +2 oxidation state.

The XPS spectra of the chromium 2p photoelectron region of the impregnated carbon samples are illustrated for comparison in Figure 4. The spectrum of CrO_3 is reported as a representative Cr(VI) compound and is not intended to imply speciation. The position of the Cr $2p_{3/2}$ photoelectron peak is indicative of chromium in the +6 oxidation state.[3,4,8] Note the broadening of the $2p_{3/2}$ peak for the carbon samples. This broadening suggests that chromium is present in more than one environment.

The binding energy of the peak obtained following subtraction (see Figure 2) is 576.0 eV, which is indicative of chromium in the +3 oxidation state. Values of chromium(VI)/total chromium were determined following the procedure described previously and are reported in Table 4. Note from the table that for both ASC and ASC-TEDA, the Cr(VI)/total Cr ratio is lower when samples were analyzed as granules as opposed to fine powders. Also, note that ASC-TEDA possesses a greater Cr(VI)/total Cr ratio than does the untreated ASC.

Table 4
Chromium(VI) to Total Chromium Ratios for Whetlerite Samples
as Determined by XPS

Sample	Cr(VI)/Total Cr
ASC (granule)	0.69
ASC (<325 mesh)	0.80
ASC TEDA (granule)	0.74
ASC TEDA (<325 mesh)	>0.90

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Figure 2. Subtraction of the CrO_3 Spectrum from the Cr Spectrum of ASC (Granules). [(A) ASC (granules), (B) CrO_3, (C) Resulting spectrum following subtraction of B from A.]

Figure 3. XPS Spectra of the Copper 2p Photoelectron Region. [(A) ASC (<325 mesh), (B) ASC (granules), (C) ASC-TEDA (> 325 mesh) and (D) CuO.]

Figure 4. XPS Spectra of the Chromium 2p Photoelectron Region. [(A) ASC (<325 mesh), (B) ASC (granules), (C) ASC-TEDA (> 325 mesh) and (D) CrO$_3$.]

Figure 5 compares the oxygen 1s spectra of the ASC carbon to that of BPL. BPL is representative of base carbon prior to impregnation. Note that the binding energy of the oxygen 1s photoelectron peak of BPL is approximately 1.5 eV greater than that of the impregnated carbons (BE = 530.8±0.1eV). Binding energies for copper, chromium and oxygen for all samples analyzed in this study are reported in Table 5.

Table 5
Elemental Binding Energies for Activated Carbon

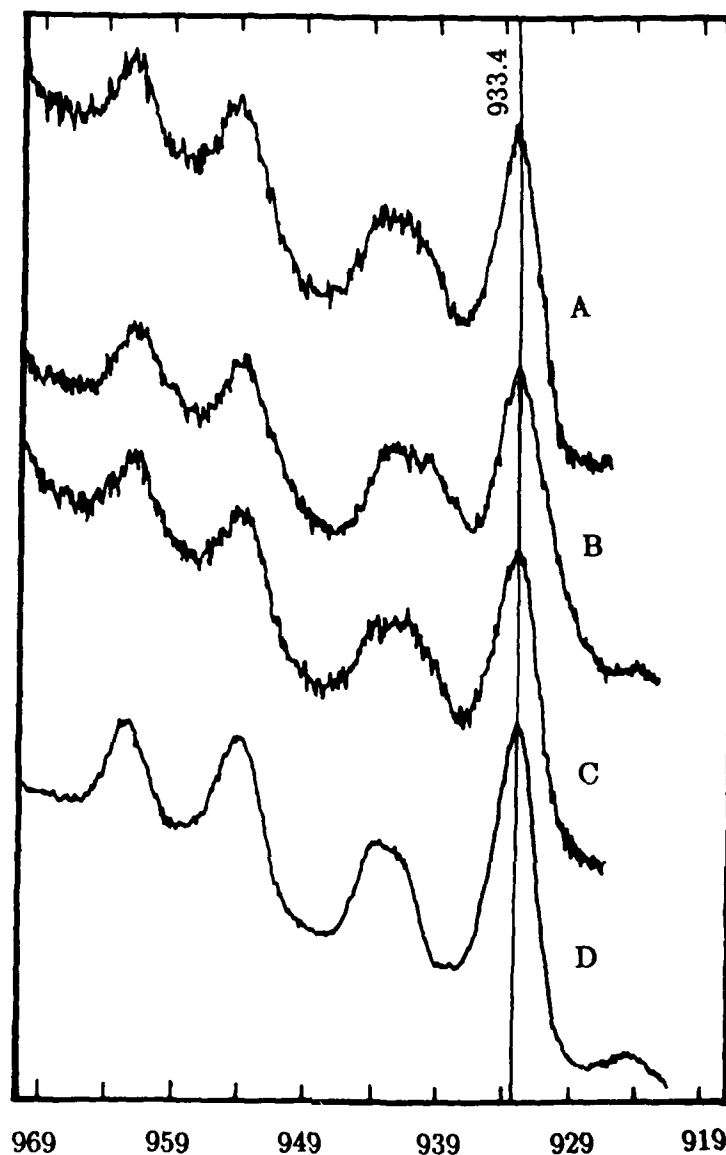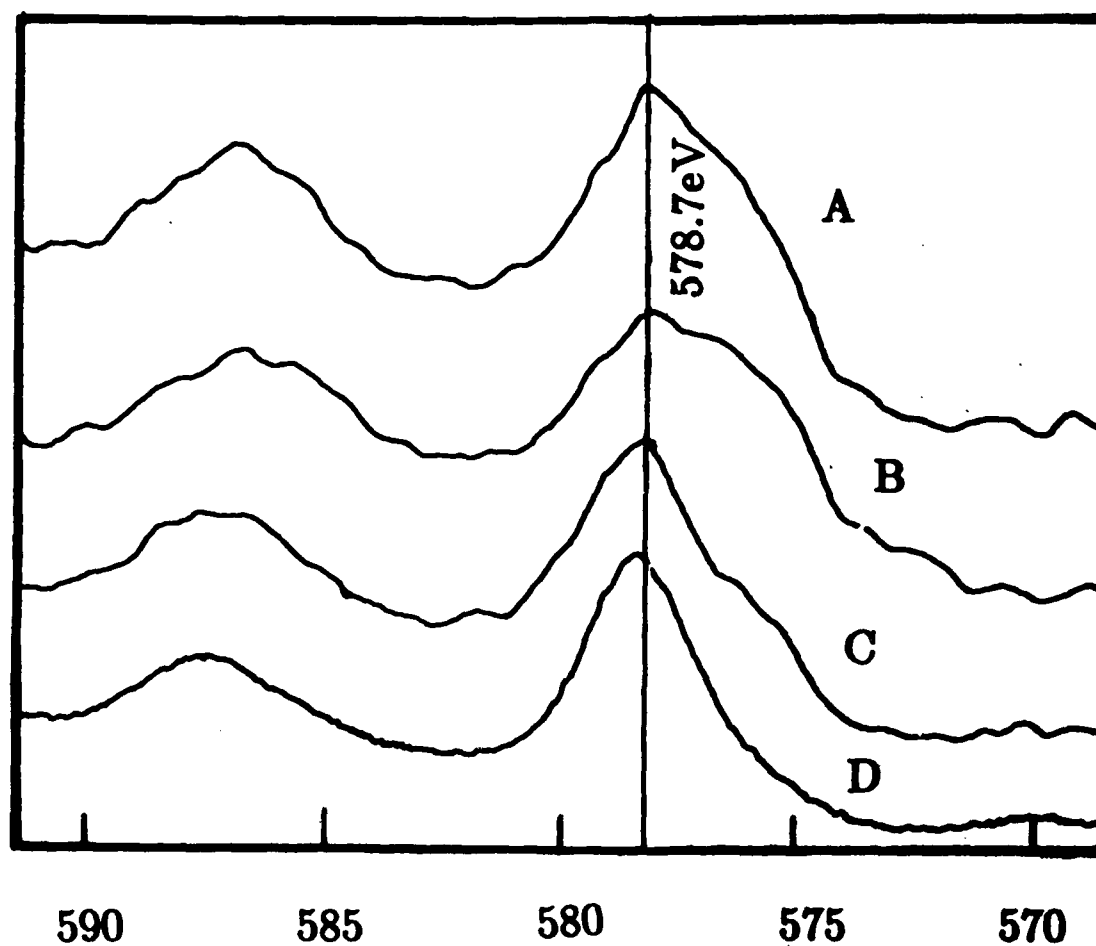| Sample	Binding Energy (eV)		
	Cu $2p_{3/2}$	Cr $2p_{3/2}$	O 1s
BPL (granule)			532.3
BPL (<325 mesh)			532.3
ASC (granule)	933.4	578.3	530.6
ASC (<325 mesh)	933.7	578.8	531.0
ASC TEDA (granule)	933.5	579.0	530.9
ASC TEDA (<325 mesh)	933.3	578.7	530.6
Hammarstrom and Sacco (3)	933.6	578.0	
CuO	933.4		529.8
CrO_3		579.0	530.4

Table 6 reports quantitative XPS and chemical analyses of the various carbon samples in the form of elemental ratios. Elemental ratios corresponding to the bulk sample were calculated using the O/C ratio determined by XPS of the corresponding crushed sample. Note that for ASC and ASC-TEDA, crushing the sample results in a decrease in the Cu/C, Cr/C and O/C ratios, however, the Cu/Cr ratio is essentially uneffected. Also, elemental ratios determined for the crushed sample agree more closely with that of the bulk chemical analysis.
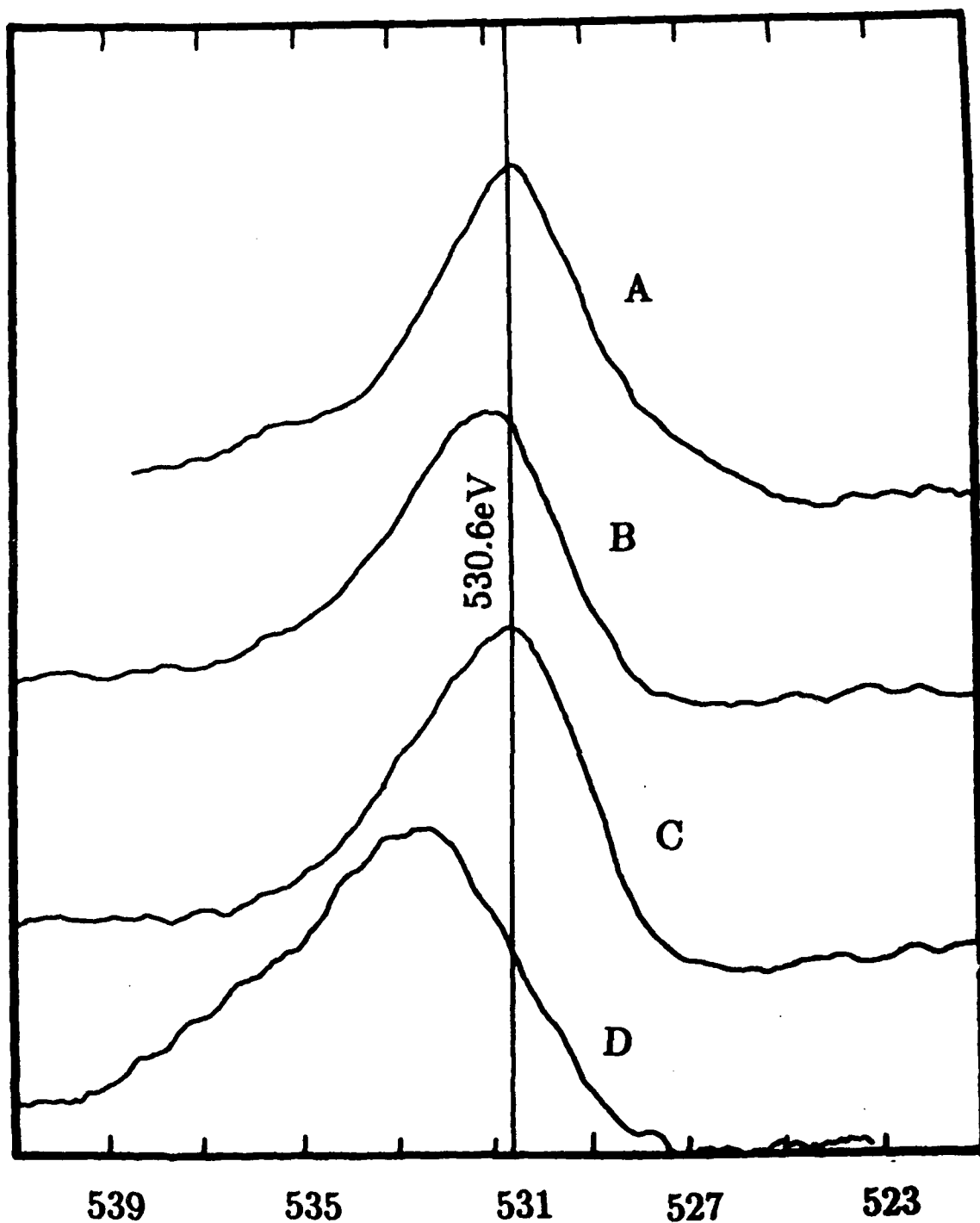
Figure 5. XPS Spectra of the Oxygen 1s Photoelectron Region. [(A) ASC (<325 mesh), (B) ASC (granules), (C) ASC-TEDA (> 325 mesh) and (D) BPL (granules).]

Table 6
Elemental Ratios as Determined by XPS

Sample	Elemental Ratios			
	Cu/C	Cr/C	O/C	Cu/Cr
BPL (granule)			0.0750	
BPL (<325 mesh)			0.0586	
ASC (granule)	0.0609	0.0298	0.2510	2.11
ASC (<325 mesh)	0.0276	0.0122	0.1250*	2.25
Chemical analysis	0.0198	0.0091	0.1250	2.18
ASC TEDA (granule)	0.0354	0.0197	0.1878	1.80
ASC TEDA (<325 mesh)	0.0221	0.0100	0.0966*	2.21
Chemical analysis	0.0192	0.0088	0.0966	2.18

* Elemental ratios determined from chemical analysis employ O/C ratio determined from XPS analysis of crushed sample.

4. DISCUSSION

XPS spectra were recorded for samples as received (12-30 mesh granules), and crushed into a fine powder. XPS provides a chemical analysis of the outer 30-50A of the sample surface exposed to the X-ray source. Crushing the granules to a fine powder results in exposing the internal regions of the granule to the X-ray source. The majority of the surface area is located within the carbon sample. Crushing the sample will expose the internals of the carbon to the X-ray source. This provides an analysis which is more representative of the entire carbon granule. Spectra of the crushed and as-received granules are compared for two reasons: first, to obtain information regarding chemical states of species at the two locations (i.e., external surface of the granule and within the particle), and second, to determine if the impregnation procedure resulted in depositing a large fraction of metals at the external surface of the granule.

4.1 Copper XPS.

A comparison of the copper 2p photoelectron region of the various carbon samples is presented in Figure 3. The spectrum of copper(II) oxide is present as a representative of copper in the +2 oxidation state and is not intended to imply

speciation. All spectra are similar, which suggests that treatment of ASC with TEDA does not alter the oxidation state of copper, at least over the age of the samples reported here. Small amounts of copper(I) and copper(0) have been reported to be present on impregnated carbons.[1,2,3] Pytlewski[1] reports that copper is predominantly present as Cu(II) complexed with chromium. Pytlewski does note the presence of copper(I) and copper(0) species. Hammarstrom and Sacco[2,3] report that approximately 80-85% of the copper associated with fresh ASC Whetlerite exists as copper(II). No evidence as to the existence of lower oxidation state species is evident from the spectra reported in Figure 3. The presence of lower oxidation states of copper is likely, but are probably not observed due to the strong copper(II) signal.

4.2 Chromium XPS.

The position of the chromium $2p_{3/2}$ photoelectron peak corresponding to the impregnated carbons indicates that chromium is in the +6 oxidation state and is consistent with results reported elsewhere.[3,4,8] The position and shape of this peak is similar to that reported by Hammarstrom and Sacco in that a strong shoulder is evident on the $2p_{3/2}$ photoelectron peak.[3,4] The shoulder is likely due to the presence of chromium in the +3 oxidation state. Following subtraction of the chromate spectrum from that of the impregnated carbons, a peak is observed at 576.0±0.2 eV (see Figure 2). The position of this peak corresponds to chromium in the +3 oxidation state.[3,8] The magnitude of the Cr(III) shoulder, along with the Cr(VI)/total Cr ratio, decreases upon crushing the impregnated carbon granules, suggesting that the fraction of chromium in the +3 and lower oxidation states at the external surface of the granule is greater than what is found within the granule. ASC-TEDA was found to possess a greater Cr(VI)/total Cr ratio than ASC. Note from Figure 4 the relatively small Cr(III) shoulder associated with the TEDA treated sample. Quantitative XPS analyses reveal that 80% of the chromium associated with the ASC Whetlerite exists as Cr(VI), while this value is increased to approximately 90% in the case of ASC-TEDA. These data suggest that treatment of ASC with TEDA either increases the fraction of chromium(VI) in the sample, or decreases the rate at which chromium(VI) species are reduced to species of lower oxidation state.

The Cr(VI)/total Cr ratios reported in Table 4 are within the range of values reported by others. Hammarstrom and Sacco[2] report ratios of 0.93 using a wet chemical extraction technique, while more recently Krishnan[5] has reported ratios of approximately 0.70 using similar extraction techniques. Using XPS, Hammarstrom and Sacco[4] report a ratio of 0.80 for fresh ASC Whetlerite, and a ratio of 0.98 for the same material using a pulse hydrogen uptake technique. Discrepancies can be attributed to not only the different techniques employed but also to the fact that different samples were used in each study.

Cyanogen chloride activity of ASC Whetlerite has been attributed to chromium(VI) complexes.[1,5,6] The greater the Cr(VI) fraction, the greater the cyanogen chloride activity one would expect. Since the Cr(VI)/total Cr ratio is increased upon treatment of ASC with TEDA, one would expect the cyanogen

chloride reactivity of ASC-TEDA to be greater than that of untreated ASC. This has in fact been observed by Groose et al.[7] Treatment of ASC Whetlerite with between 1.5 and 3.0 wt% TEDA increased the cyanogen chloride breakthrough time an average of 18% for 3 different ASC samples.

4.3   Oxygen XPS.

Results presented in Figure 5 and in Table 6 suggest that a large fraction of oxygen is associated with the metals, which is to be expected based on speciation reported by Pytlewski.[1] The oxygen 1s binding energy of 530.8 eV for impregnated carbons is consistent with that reported for oxides of chromium and copper,[8] while the binding energy of 532.2 eV for BPL agrees well with values reported by Marchon et al.[9] for graphite. In addition, the oxygen to carbon ratios for the impregnated carbons are significantly greater than those calculated for BPL. No overlap of the peaks is evident from Figure 5; however, the spectra of ASC granules, which possesses the highest O/C atomic ratio, is rather symmetrical, while the spectra corresponding to the crushed impregnated carbons appears to tail to high energy. This asymmetrical shape is likely due to the overlap of the two oxygen peaks.

4.4   Quantitative XPS Analyses.

Quantitative XPS analyses, in the form of elemental ratios, are used to determine whether the impregnation process placed the metal within the pore network of the material, or deposited a large fraction of metal onto the external surface.[10,11,12] Comparing the metal/C ratio determined by XPS to that determined by chemical analysis (provided by the manufacturer in this case) will provide the above information. If the metal/C ratio determined from analysis of the granule is many times larger (30 or more) than that determined by chemical analysis, virtually all the metal will be located on the external surface of the granule.[12] If the metal/C ratio is approximately equal to that determined by chemical analysis, indications are that the vast majority of the metal is located within the granule. Quantitative XPS analyses, reported in Table 6, reveal the following regarding the location of the impregnants. Note from the analysis of ASC granules that the Cu/C and Cr/C atomic ratios are approximately three times greater than the corresponding bulk analysis. This indicates that the outer regions of the granules, following preparation, are rich in impregnants, and thus the impregnant distribution is not radially uniform.[12] ASC Whetlerite is impregnated as 12-30 mesh granules from solutions of copper and chromium complexes. It is reasonable that, due to the rather large size of the granules, impregnants would accumulate in greater concentrations at the outer regions of the granules. For ASC treated with TEDA, the Cu/C and Cr/C ratios determined for the granules are approximately half those of the untreated ASC. This suggests that treatment with TEDA reduces the metal accumulation at the external surface of the granule. Cu/C and Cr/C ratios calculated from analyses of the crushed granules are more representative of the bulk analysis, but slightly greater. It is also interesting to note that despite the external surface enrichment of the granule with impregnants, that the Cu/Cr ratios for both ASC and ASC-TEDA are in excellent agreement with those obtained from chemical analysis. This is

somewhat surprising, as one may expect copper and chromium to occupy different locations, due to the difference in their respective concentrations (8% copper and 3% chromium).

5. CONCLUSIONS

Copper exists primarily in the +2 oxidation state on both ASC and ASC treated with TEDA. Lower oxidation state species of copper were not observed using XPS.

Chromium (VI) and chromium (III) species are observed on ASC and ASC-TEDA by XPS. For both materials, the ratio of Cr(VI) to total Cr is lower at the external surface of the granule relative to the ratio determined upon analysis of the crushed sample.

XPS analysis may be used to determine quantitative Cr(VI)/total Cr ratios. This is accomplished by subtraction of CrO_3 from the ASC chromium spectrum.

Following impregnation, the external surface of the ASC and ASC-TEDA granules are rich in impregnants relative to the bulk. However, the Cu/Cr atomic ratio at the external surface and within the granule as determined by XPS are consistent with the chemical analysis.

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APPENDIX
Collection of Raw Data

Table A-1
XPS Analysis of BPL Carbon

Sample: BPL Carbon, Lot # 7502

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	274.2	37,595	284.6	150,380
O 1s	524.5	7,555	532.3	11,276

Elemental Ratios:

O/C   0.0750

Table A-2
XPS Analysis of Crushed BPL Carbon

Sample: Crushed BPL Carbon (<325 mesh), Lot # 7502

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	275.5	40,160	284.6	
O 1s	525.8	6,304	532.3	

Elemental Ratios:

O/C   0.0586

Table A-3
XPS Analysis of ASC Granules

Sample: ASC Carbon, Lot # 1667

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	278.5	188325	284.6	75,328
Cr		5000		2,174
$2p_{1/2}$	583.7		586.6	
$2p_{3/2}$	575.3		578.3	
Cu		30732		4,587
$2p_{1/2}$	955.1		954.2	
$2p_{3/2}$	934.1		933.4	
O 1s	527.1	12760	530.6	18,910

Elemental Ratios:

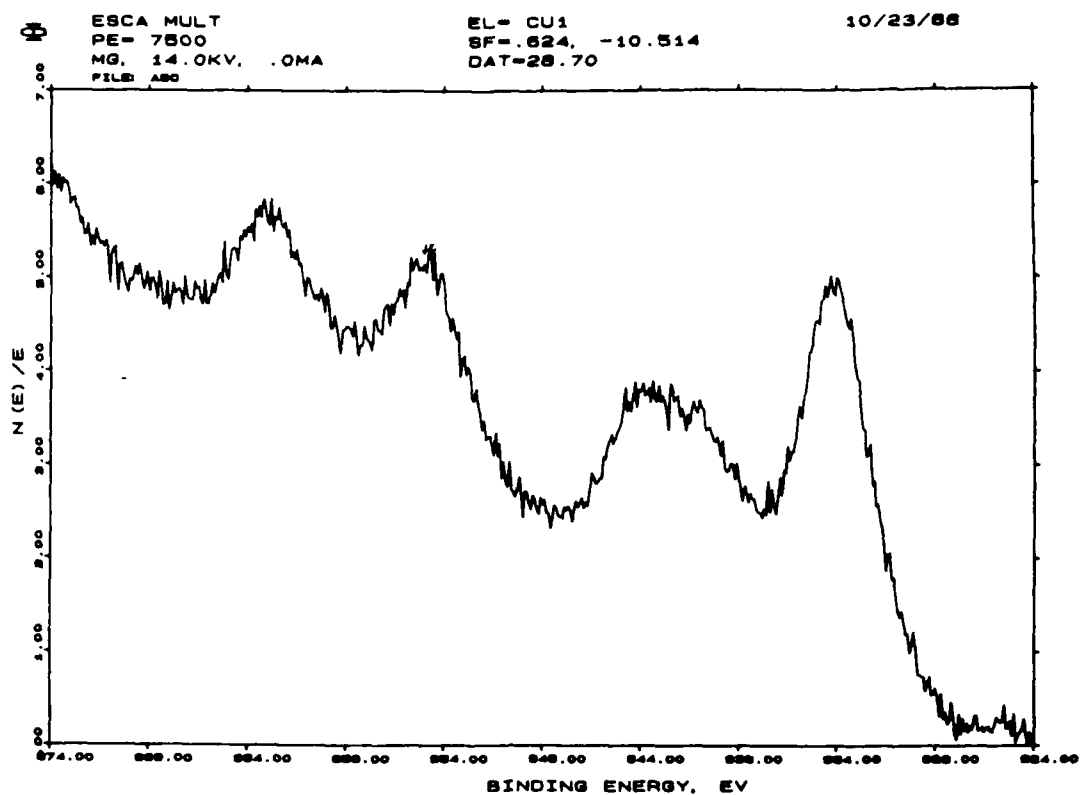|	
Cu/C	0.0609
Cr/C	0.0289
O/C	0.2510
Cu/Cr	2.110

Figure A-1. XPS Spectrum of the Copper 2p Photoelectron Region of ASC Granules.
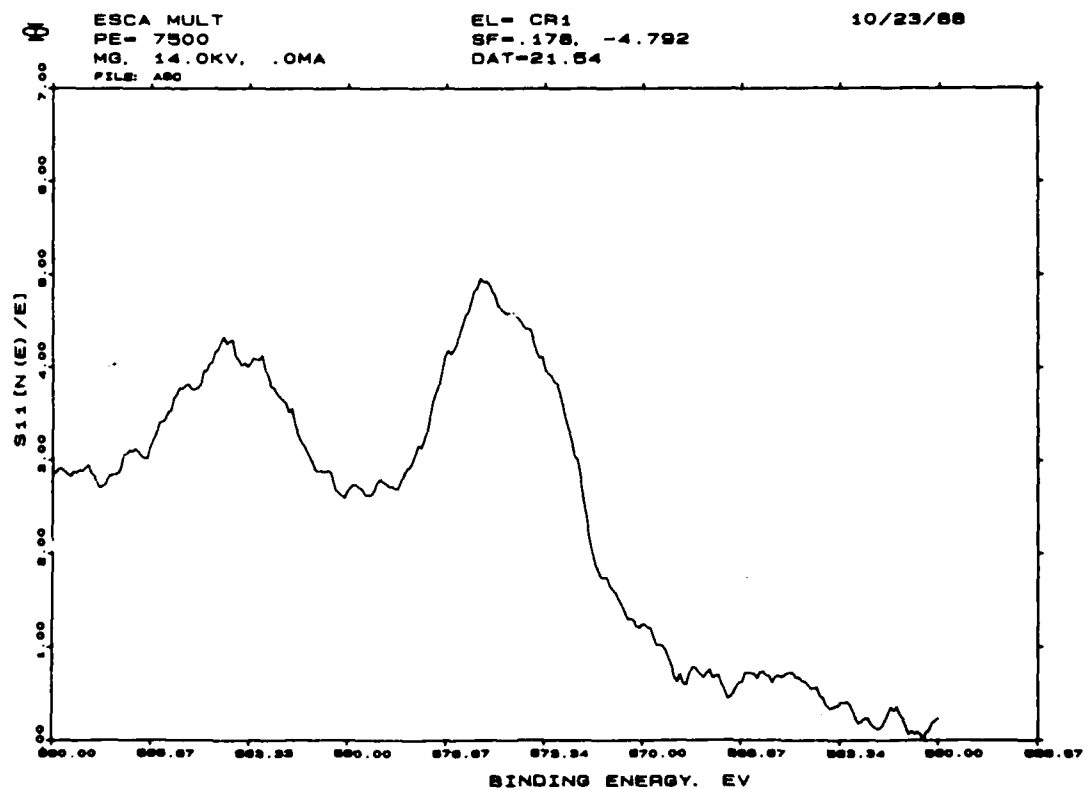

Figure A-2. XPS Spectrum of the Chromium 2p Photoelectron Region of ASC Granules.

Table A-4
XPS Analysis of ASC Crushed to <325 Mesh

Sample: Crushed ASC Carbon, Lot # 1667

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	275.8	39,898	284.6	159,592
Cr		4,484		1,949
$2p_{1/2}$	581.7		587.3	
$2p_{3/2}$	572.9		578.6	
Cu		30,009		4,479
$2p_{1/2}$	952.6		954.4	
$2p_{3/2}$	931.5		933.5	
O 1s	524.7	13,831	530.9	20,643

Elemental Ratios:

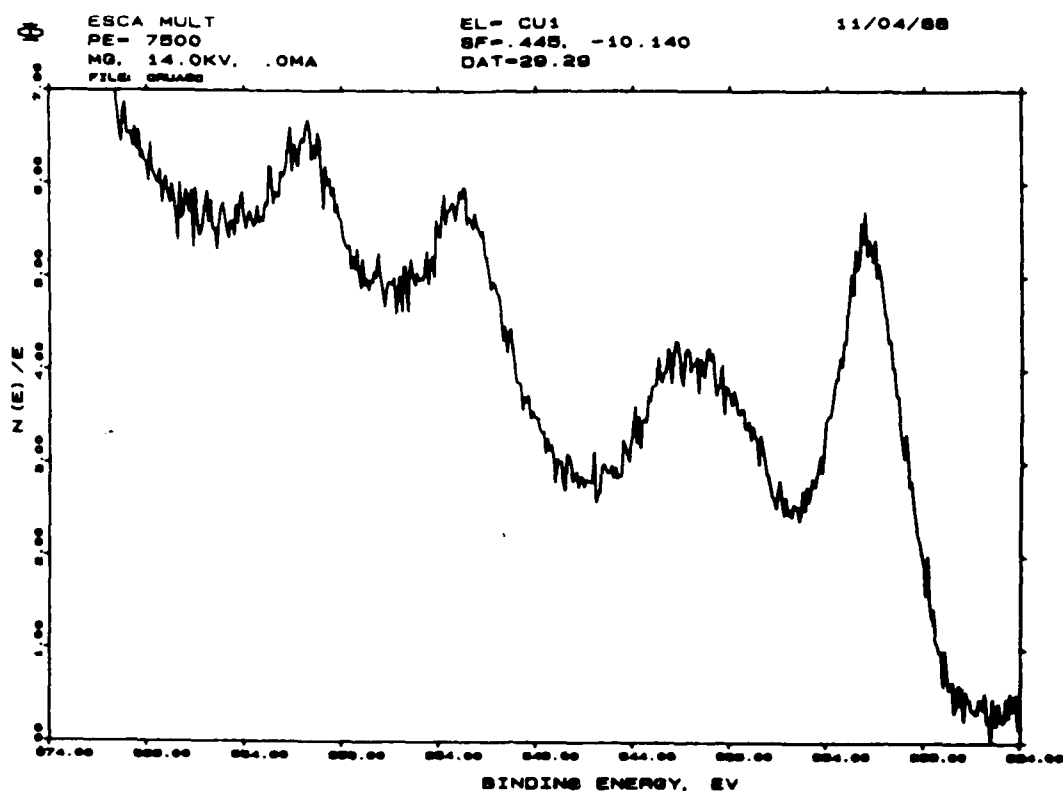|	
Cu/C	0.0281
Cr/C	0.0122
O/C	0.1294
Cu/Cr	2.297

Figure A-3. XPS Spectrum of the Copper 2p Photoelectron Region of ASC Granules Crushed to < 325 Mesh.
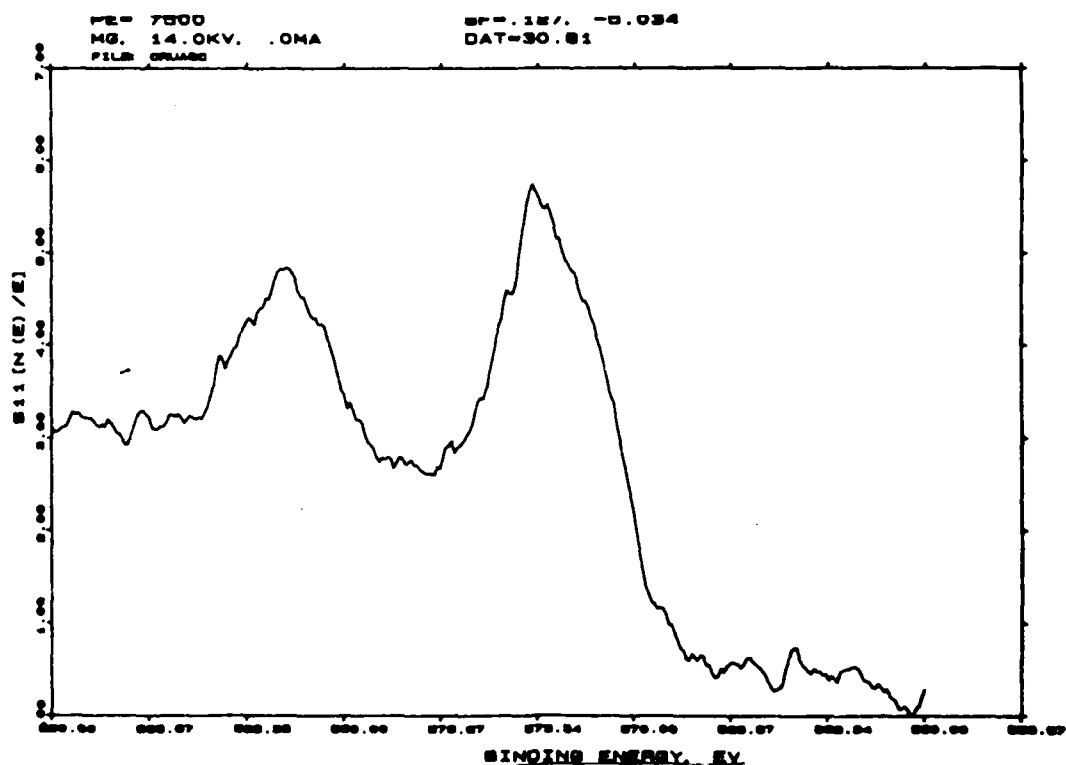

Figure A-4. XPS Spectrum of the Chromium 2p Photoelectron Region of ASC Granules Crushed to < 325 Mesh.

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Table A-5
XPS Analysis of ASC Crushed to <325 Mesh

Sample: Crushed ASC Carbon, Lot # 1667

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	276.0	29,708	284.6	118,832
Cr		3,347		1,455
$2p_{1/2}$	582.0		587.4	
$2p_{3/2}$	573.5		579.0	
Cu		21,948		3,276
$2p_{1/2}$	952.6		954.2	
$2p_{3/2}$	932.0		933.8	
O 1s	525.0	9,951	531.0	14,852

Elemental Ratios:

Cu/C	0.0276
Cr/C	0.0122
O/C	0.1250
Cu/Cr	2.251

Sample: ASC-TEDA Carbon, Lot # 794

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	277.2	25,282	284.6	101,128
Cr		4,577		1,990
$2p_{1/2}$	583.0		587.2	
$2p_{3/2}$	574.7		579.0	
Cu		24,017		3,585
$2p_{1/2}$	954.0		954.4	
$2p_{3/2}$	932.9		933.5	
O 1s	526.1	12,726	530.9	18,944

Elemental Ratios:

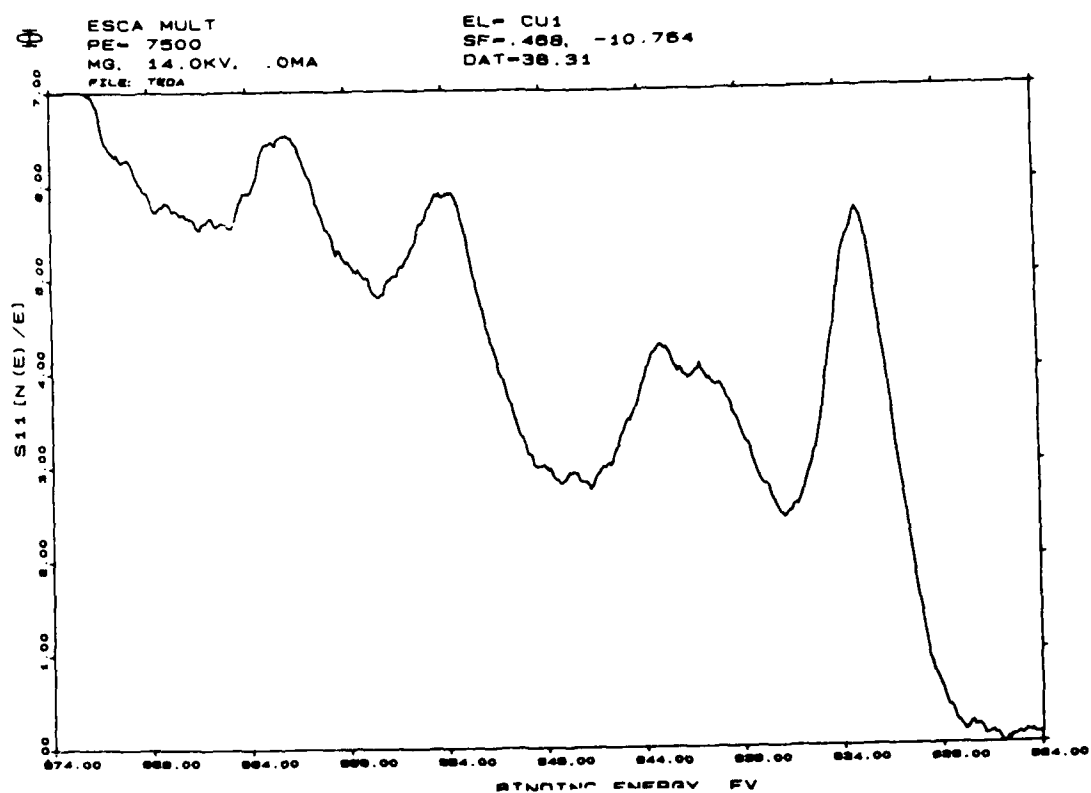|	
Cu/C	0.0354
Cr/C	0.0197
O/C	0.1878
Cu/Cr	1.8013

Figure A-5. XPS Spectrum of the Copper 2p Photoelectron Region of ASC-TEDA Granules.

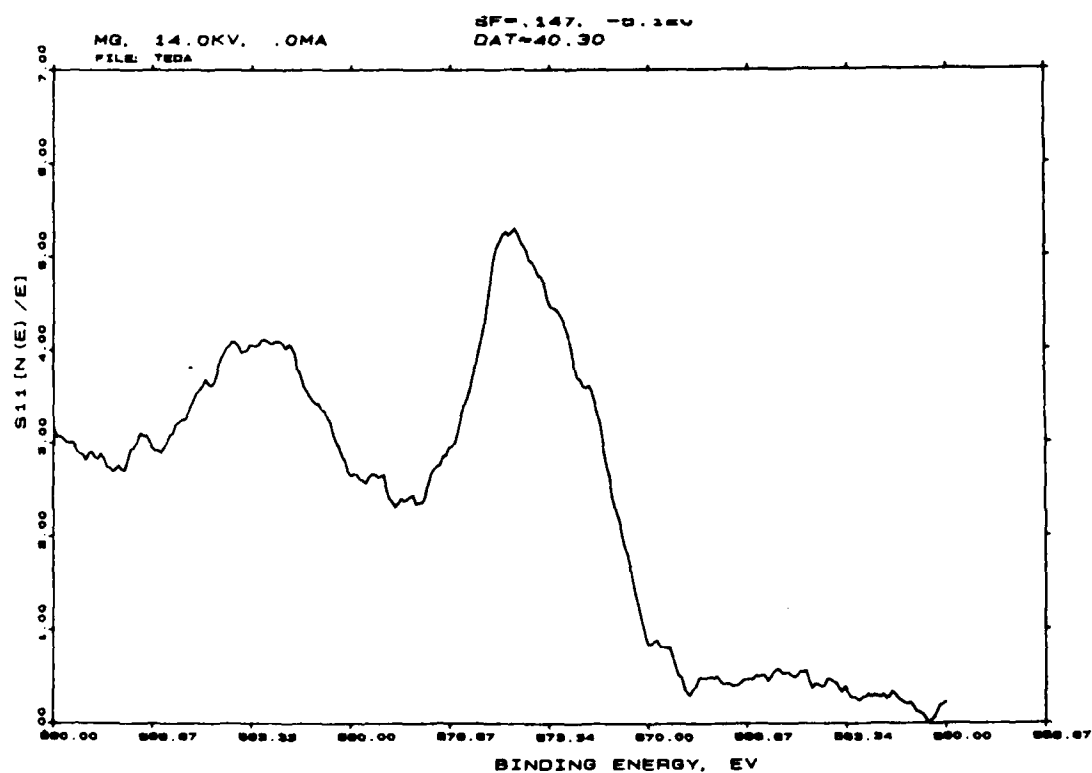**Figure A-6.** XPS Spectrum of the Chromium 2p Photoelectron Region of ASC-TEDA Granules.

Table A-7
XPS Analysis of ASC-TEDA Crushed to < 325 Mesh

Sample: Crushed ASC-TEDA Carbon (<325 mesh), Lot # 794

Element	B.E. (eV)	Area	Corr B.E. (eV)	Corr Area
C 1s	274.5	36,876	284.6	147,584
Cr		3,386		1,473
$2p_{1/2}$	581.4		587.4	
$2p_{3/2}$	572.6		578.7	
Cu		21,812		3,255
$2p_{1/2}$	952.0		954.2	
$2p_{3/2}$	930.9		933.3	
O 1s	524.2	9,544	530.8	14,245
N 1s	393.1		401.3	

Elemental Ratios:

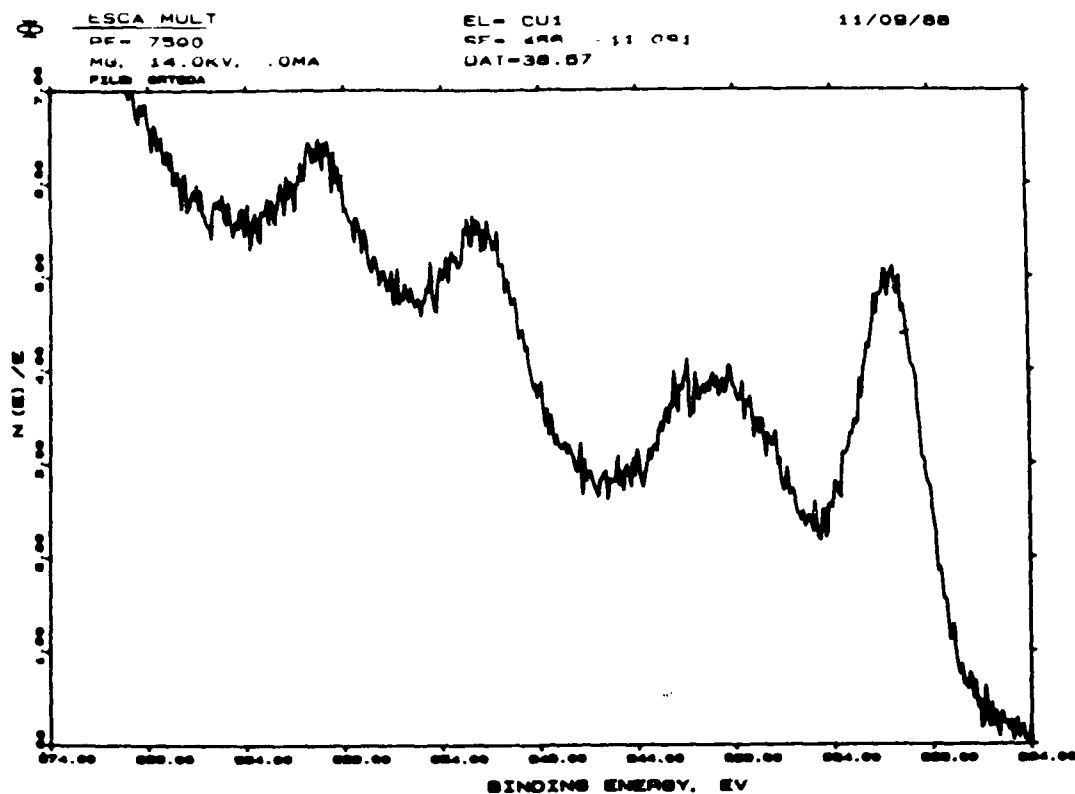|	
Cu/C	0.0221
Cr/C	0.0100
O/C	0.0966
Cu/Cr	2.21

Figure A-7. XPS Spectrum of the Copper 2p Photoelectron Region of ASC-TEDA Granules Crushed to < 325 Mesh.
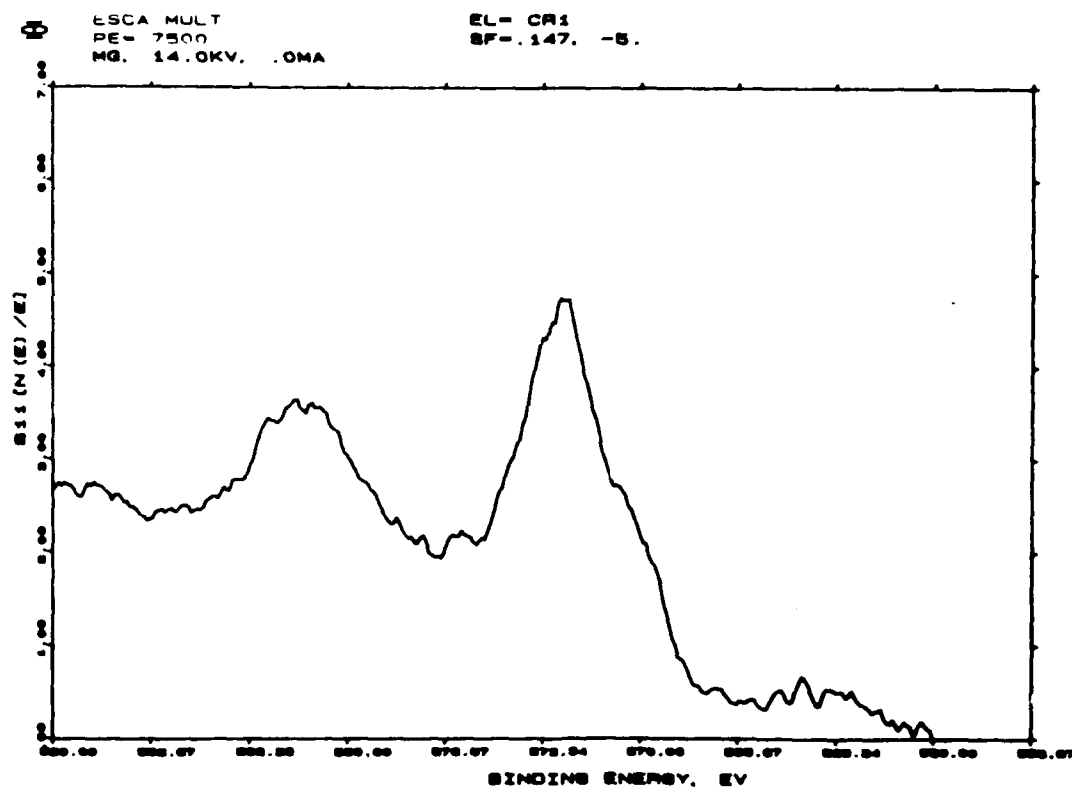

Figure A-8. XPS Spectrum of the Chromium 2p Photoelectron Region of ASC-TEDA Granules Crushed to < 325 Mesh.